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An attempt to compare the performance of bioscrubbers and biotrickling filters for degradation of ethyl acetate in gas streams

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Abstract: This study presents a comparison of the efficiency of a bioscrubber and a biotrickling filter (BTF) for the removal of ethyl acetate (EA) vapour from a waste gas stream, under the same operating conditions. The maximum EA elimination capacity achieved in the bioscrubber was 550 g m^{-3} h^{-1} with removal efficiency higher than 96%. For higher EA loadings the bioscrubber was oxygen limited, which caused incomplete EA biodegradation. When pure oxygen was fed to the bioscrubber at a rate of 0.02 L min^{-1}, the bioscrubber recovered and could treat higher EA loadings without any oxygen limitation. The BTF achieved EA elimination capacity of 600 g m^{-3} h^{-1} with removal efficiency higher than 97% and the dissolved oxygen concentration remained substantially higher than in the bioscrubber. However, severe channelling and blockage of the spray nozzle occurred due to the excessive biomass growth. Overall, the bioscrubber system was easier to operate and control than the BTF, while an enhancement of the oxygen mass transfer in the bioscrubber could potentially increase its performance by up to three times.

Keywords: ethyl acetate; bioscrubber; biotrickling filter; oxygen limitation

NOTATION

BTF	Biotrickling filter
$C_{in_{EA}}$	Influent gas ethyl acetate concentration (g L^{-1})
$C_{out_{EA}}$	Effluent gas ethyl acetate concentration (g L^{-1})
$C_{L_{O_2}}$	Dissolved oxygen concentration (g L^{-1})
$C^*_{O_2}$	Steady state saturated dissolved oxygen concentration (g L^{-1})
CSTR	Continuous stirred tank reactor
EA	Ethyl acetate
G	Gas flow rate (L h^{-1})
$K_L a_{O_2}$	Volumetric mass transfer coefficient for oxygen (h^{-1})
$MW_{biomass}$	Biomass molecular weight ($g_{biomass}$ $mol_{biomass}{}^{-1}$)
N_{EA}	Ethyl acetate flux (g h^{-1})
N_{O_2}	Oxygen flux (g h^{-1})
rpm	Revolutions per minute
TOC	Total organic carbon (g_{carbon} L^{-1})
V	Biomedium volume (L)
$Y_{X/EA}$	Biomass yield factor ($mol_{biomass}$ $mol_{EA}{}^{-1}$)

INTRODUCTION

There is a wide range of well-established chemical and physical approaches that have been applied to control volatile organic compound (VOC) emissions, such as incineration, catalytic oxidation or activated-carbon adsorption. These technologies have a number of drawbacks, among which the most important is the high cost.[1] Competitive alternatives to chemical or physical approaches are biological waste gas treatment technologies such as bioscrubbing and biotrickling filtration.

The use of ethyl acetate (EA) as a solvent in pharmaceutical applications, in artificial fruit essences, and in the manufacture of smokeless powder, artificial leather, photographic films and cleaning textiles, results in its release to the environment through various waste streams.[2] Since EA is an easily biodegradable compound, biotechnology offers an attractive opportunity to tackle EA emissions, and EA biodegradation has been applied so far in biofilters[3,4] and biotrickling filters (BTFs).[5,6]

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Bioscrubbing and biotrickling filtration are nowadays two competing technologies in the field of waste gas biotreatment. The aim of this study is to compare the efficiency of bioscrubbing and biotrickling filtration technologies for removal of EA vapours from a waste gaseous stream, under the same operating conditions.

Bioscrubbing

In bioscrubbers, the target VOC is absorbed into and then biodegraded in an aqueous liquid phase in a bioreactor containing suspended cells. The control of the bioscrubbing process is straightforward through the control of the liquid medium composition and the prevention of any inhibitory effects by washing out of the inhibitory compound. Bioscrubbing is a competitive process to biofiltration and its operating costs are from one-half to one-fourth of the operating costs of a chemical scrubber.[1] On the other hand, mass transfer limitations may occur when dissolving the VOC into the aqueous phase.[7] Bioscrubbing gives better results when the VOC fed is highly water-soluble, and mass transfer resistances for the VOC are lower. In some cases, the rate-limiting step is biodegradation, but when the system has a very high biomass concentration, diffusion can be considered as the rate-limiting step of the process. Hecht *et al*[8] observed that for trichloroethylene (TCE) biodegradation in a bioscrubber the rate-limiting step of the process was biodegradation rather than TCE mass transfer.

Bioscrubbing has been applied for the removal of odorous sulfur compounds such as hydrogen sulfide[1,8] and for the removal of VOCs,[8–10] and generally provides much higher VOC removal efficiencies than biotrickling filtration. Oliveira and Livingston[11] treated a monochlorobenzene (MCB)-containing gas stream in a bioscrubber, reaching elimination capacities of 450 g MCB m^{-3} h^{-1}, a number which is substantially higher than the MCB maximum elimination capacities reported for BTFs and biofilters (60 g m^{-3} h^{-1}).[12] These elimination capacities are much higher than those achieved with BTFs for compounds 'easier' to degrade than MCB, such as toluene (68–112 g m^{-3} h^{-1} with 78–99% removal efficiency).[12]

Biotrickling filtration

Biofilters consist of packed beds of solids on the surface of which biofilms of microbial consortia are formed. Due to the fact that biofilters provide poor control of nutrients and pH in the packed column, engineers modified them by the addition of a liquid-fill bioreactor to give a system referred to as a biotrickling filter (BTF). BTFs are beds packed with well-specified, non-porous inorganic particles. A liquid stream trickles through the bed of solids, providing nutrients to the biofilm and returns to the bioreactor, which serves as a pH control and nutrients-addition vessel. Due to the better nutrients and pH control, and the larger air–liquid interfacial area, VOC removal rates in BTFs are substantially higher than the rates obtained with biofilters.[13,14] The higher removal rates and the better reactor control,[15] imply substantially lower bioreactor sizes (lower capital cost) and have caused a shift in interest from biofilters to BTFs in the past few years even though instrumentation and operational costs are higher. BTFs have been also applied to the removal of hydrogen sulfide from odours.[16] The main limitation of BTFs is the excessive growth of biomass formed under high VOC loadings. Biomass clogs the packed bed and channelling occurs, leading to reduction of the interfacial area and mass transfer inhibition.[7] This accumulation of biomass requires periodic removal to avoid too high a pressure drop in the bed.[15] BTFs have long start-up periods that could last for several days, and in the event of cell activity loss, an additional start-up period may be required.[17]

MATERIALS AND METHODS

Experimental set-up

A schematic diagram of the bioscrubber apparatus is presented in Fig 1(A). An air stream controlled by a TYLAN RO-28 (West Technologies Systems Ltd, Bristol, UK) mass flow controller was enriched with EA by passing it via a sintered glass sparger through a 0.25 L saturation vessel containing EA. The EA-laden stream was then mixed with a second air stream to give a constant inlet flow rate of 2 L min^{-1} to the bioreactor, resulting in an empty bed residence time (EBRT) value of 0.9 min. The inlet flow rate was kept constant while the two individual gas flow rates varied to give the required EA inlet concentration. The gas was distributed in the aqueous phase/biomedium via a stainless steel sparger. Two impellers rotating at 800 rpm (a 'marine' impeller at the bottom of the shaft and a Rushton impeller at the middle of the biomedium height), provided optimal mixing of the two phases. The bioreactor (CSTR) was an SGI 30/SET002 (Setric, Toulouse, France) model, which had a total volume of 1.8 L and was operated with 1 L liquid volume. The mineral medium was prepared in 10 L batches and its composition was 1360 mg dm^{-3} KH_2PO_4, 5370 mg dm^{-3} Na_2HPO_4, 5000 mg dm^{-3} $(NH_4)_2SO_4$, 200 mg dm^{-3} $MgSO_4.7H_2O$ and 5 dm^3 m^{-3} trace elements solution. The composition of the trace elements solution was 530 mg dm^{-3} $CaCl_2$, 200 mg dm^{-3} $FeSO_4.7H_2O$, 10 mg dm^{-3} $ZnSO_4.7H_2O$, 10 mg dm^{-3} H_3BO_3, 10 mg dm^{-3} $CoCl_2.6H_2O$, 4 mg dm^{-3} $MnSO_4.5H_2O$, 3 mg dm^{-3} $Na_2MoO_4.2H_2O$, and 2 mg dm^{-3} $NiCl_2.6H_2O$. The mineral medium was fed to the bioreactor continuously via a Watson Marlow 205S peristaltic pump (Watson Marlow Bredel Pumps Ltd, Birmingham, UK) giving a dilution rate of 0.06 h^{-1}. The pH was controlled at 7 ± 0.05 by the addition of H_2SO_4 (2 M) or NaOH (2 M), temperature was kept constant at 25 °C and the dissolved oxygen concentration was monitored with an Ingold oxygen probe (Mettler-Toledo Ltd, Leicester, UK). The gas

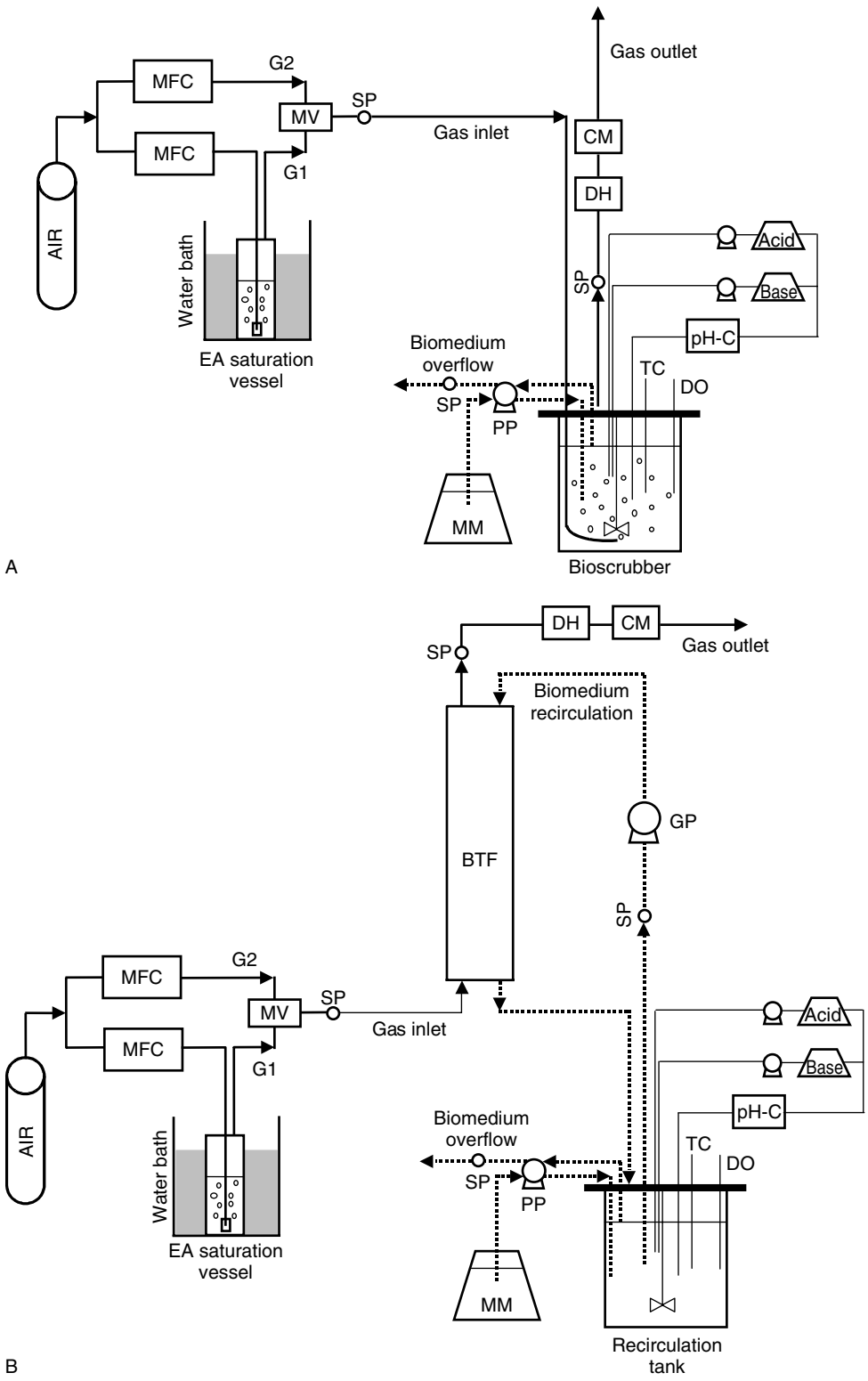

Figure 1. Schematic diagram of bioreactor apparatus: (A) bioscrubber and (B) BTF. BTF: Biotrickling filter; CM: CO_2 meter; DH: dehumidifier unit; DO: dissolved oxygen meter; G1, G2: gas streams; GP: gear pump; MFC: mass flow controller; MM: mineral medium; MV: mixing vessel; pH-C: pH controller; PP: peristaltic pump; SP: sampling port; TC: temperature controller.

outlet was connected to a carbon dioxide meter (SERVOMEX IR Gas Analyser PA 404, Servomex Group Ltd, East Sussex, UK) for monitoring of the carbon dioxide produced due to EA biodegradation.

The mixed culture that utilised EA as a sole carbon source was obtained from Membrane Extraction Technology Ltd (London, UK) (http://www.membrane-extraction-technology.com). Subcultures were prepared in shake flasks with 100 mL mineral medium containing 170 mg dm^{-3} EA, incubated at 30 °C on an orbital incubator (Gallenkamp, Loughborough, UK) at 200 rpm, and used for bioreactor inoculation before each experiment.

A schematic diagram of the BTF apparatus is presented in Fig 1(B). Since the comparison of the performance of the two systems was made under the same operating conditions, most of the operating parameters are the same as before. The EA-contaminated air stream was introduced at the same flow rate ($2\,L\,min^{-1}$) at the bottom of the column this time and not in the CSTR as before, giving an EBRT value of 1.4 min. The dimensions of the column were 70 cm height, 7.5 cm id and filled up to 65 cm with polypropylene pall rings, size 5/8″ and surface area $319\,m^2\,m^{-3}$ (Eta Process Plant, Stoke on Trent, UK).

The recirculation tank (same CSRT as before) was stirred at 800 rpm and was used for pH (7 ± 0.05) and temperature (25 °C) control. A gear pump was used for recirculation of the biomedium through the column at $0.5\,L\,min^{-1}$ countercurrent to the gas stream. The mineral medium used had the same composition and it was supplied at the same flow rate as for the bioscrubber, resulting in a dilution rate of $0.06\,h^{-1}$. The dissolved oxygen concentration and the CO_2 emissions were monitored as for the bioscrubber. For both experimental set-ups the same equipment was used.

The oxygen availability analysis was performed by the 'dynamic method of gassing out' described by Taguchi and Humphrey.[18]

Analytical procedures

For the determination of EA and ethanol concentrations both in gas and liquid streams, a Perkin Elmer Gas Chromatograph (GC) was used. The chromatograph was equipped with a Flame Ionisation Detector (FID) and a 30 m long column (Alltech AT™-5) with 0.53 mm internal diameter. The stationary phase of the column was 5% phenyl- and 95% methyl-polysiloxane (1.5 μm), while the mobile phase used was helium. Biomedium samples were centrifuged for 10 min at 13 000 rpm and the supernatant solution was filtered through 0.2 μm filters to remove any residual cells. One μL of the sample was injected into the GC. For the gas samples no pre-treatment was needed, thus 0.4 mL of gas sample was injected in the GC. The temperature of the column was kept constant at 40 °C for 7 min when an aqueous sample was injected and at the same temperature for 3 min for gas samples. The coefficient of variation for four samples was 3% at a concentration level of $500\,mg\,L^{-1}$.

For the dry cell weight determination, 5 mL of biomedium were dried in the oven for 3 days at 105 °C. Then the samples were transferred to the furnace and kept for 1 h at 600 °C to remove the organic content of the dry sample. The difference in the sample weight before and after the treatment in the furnace gave the dry cell weight contained in a 5 mL sample. Biomedium samples were also measured for absorption at 660 nm on a UV-VIS spectrophotometer (UNICAM). Thus, a calibration curve correlating the spectrophotometer reading at 660 nm to the dry cell weight was prepared. The coefficient of variation for four samples was 15%. The elemental composition for bacteria was derived from the work of Bailey and Ollis.[19]

The total organic carbon (TOC) was measured with a Shimadzu 5050 total organic carbon analyser. The biomass and any remaining solids were removed from the biomedium with centrifugation and filtration as described before. The samples were diluted with distilled water at an organic carbon concentration lower than $1000\,mg\,L^{-1}$. The coefficient of variation for three samples was 0.5%.

The anion and cation concentrations were also estimated. The analysis was performed with an Ion Chromatograph Dionex DX-120 coupled to a Dionex AS40 automated sampler. The anions column was an IonPac AS14 (4*250 mm) and the carrier liquid 3.5 mM Na_2CO_3/1 mM $NaHCO_3$. The cations column was an IonPac CS12A and the carrier liquid was 19 mM CH_4O_3S (methanesulfonic acid). The anions that could be detected were: fluoride, acetate, chloride, nitrite, bromide, nitrate, phosphate and sulfate. The cations that could be detected were: lithium, sodium, ammonium, potassium, magnesium and calcium.

All the chemicals used in this study were obtained from Sigma-Aldrich (UK), including the antifoaming agent (Antifoam 204, Organic). EA, >99% pure was obtained from Merck (UK). All chemicals were used as supplied.

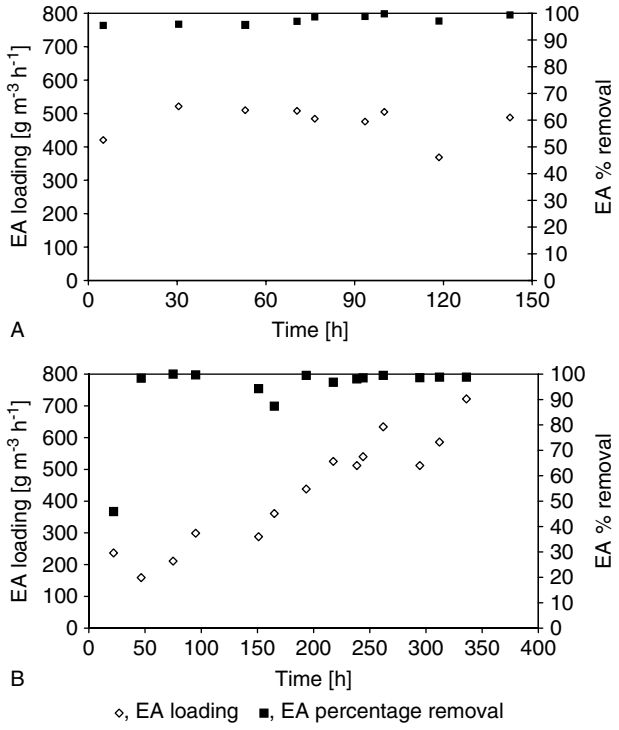

Figure 2. EA loading and percentage removal in: (A) bioscrubber and (B) BTF.

RESULTS AND DISCUSSION

Bioscrubber Operation

The EA loading and percentage removal achieved in the bioscrubber over time are presented in Fig 2(A). For an average EA loading of $500\,g\,m^{-3}\,h^{-1}$ fed over a 150 h time period, the bioscrubber exhibited EA percentage removal constantly higher than 96%. At the highest loading rate applied of $570\,g\,m^{-3}\,h^{-1}$ a maximum elimination capacity of $550\,g\,EA\,m^{-3}\,h^{-1}$ was achieved. The initial biomass concentration was $4\,g\,L^{-1}$ and the system adapted immediately to the $400\,g\,EA\,m^{-3}\,h^{-1}$ initial loading fed. So, in the beginning of the bioscrubber operation no start-up period was needed. The biomass concentration varied as a function of the EA loading over time, but for an average EA loading of $500\,g\,m^{-3}\,h^{-1}$ the biomass concentration was $5\,g\,L^{-1}$.

For the bioscrubber operation, a carbon mass balance was constructed (Figs 3(A) and 4(A)), showing the contribution of different products to the carbon outlet of the system. The process was foam-producing, and so an organic antifoaming agent was added to the biomedium manually every day. Thus, the carbon fed to the system consisted of (i) the organic carbon contained in the antifoaming agent and (ii) the EA carbon content. The effluent carbon consisted of the carbon discharged due to: (i) CO_2 produced, (ii) biomass produced, (iii) EA in the gas outlet and (iv) TOC in the biomedium. Figure 4(A) shows that the carbon fed was almost completely converted to

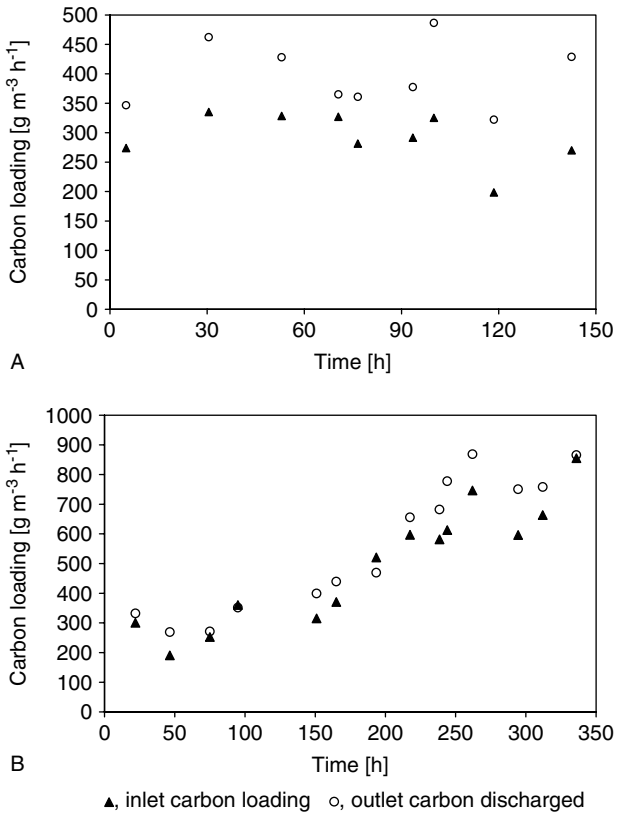

Figure 3. Carbon mass balance in: (A) bioscrubber and (B) BTF.

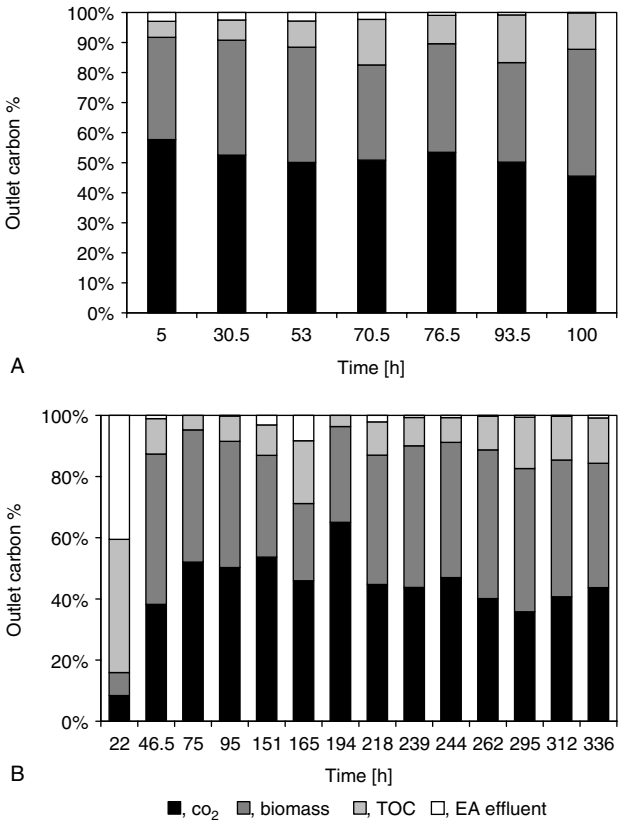

Figure 4. Carbon mass balance in: (A) bioscrubber and (B) BTF. Percentages of: (i) CO_2, (ii) biomass, (iii) TOC and (iv) EA effluent in the carbon outlet.

CO_2 and biomass. The average percentages of carbon in CO_2 and biomass, as compared with the total carbon outlet, were 52% and 36% respectively. Thus, 88% of the effluent carbon was due to these two parameters. On the other hand, only 12% of the effluent carbon was due to EA that had not been treated (2%) or TOC (10%). The antifoaming agent fed was non-biodegradable and could increase TOC by only $\sim 13\,g\,C\,m^{-3}\,h^{-1}$ (20–25% of the measured TOC). Thus the residual TOC must be due to another reason. Further GC analysis of the gas and liquid samples detected and identified the presence of ethanol in both phases. Ethanol is an expected intermediate product in the EA degradation metabolic pathway and this result is in agreement with previous studies,[20] which suggested that the first biodegradation step is EA hydrolysis to ethanol and acetic acid. Isolation and purification of an enzyme—acetylesterase—which performs the hydrolysis has been reported in previous studies.[20] The appearance of ethanol could be also partially due to a chemical hydrolysis of EA in water. No traces of acetic acid were detected in the biomedium, however NaOH was added continuously throughout the process, which is a clear indication of acid production. For example in 8 days of operation the system utilised ~1 mol of EA and consumed ~0.6 mol of NaOH. It is also important to note that acetic acid is a much more readily biodegradable compound than ethanol. For example the reported half-life of ethanol in surface water is in

the range of 6.5–24 h,[21] while for the acetic acid, a half-life as short as 24 min has been reported.[22] In addition there is evidence that the metabolic pathway of ethanol biodegradation produces acetic acid/acetate (or a derivative) as an intermediate.[23] Thus we speculate that ethanol biodegradation is the slowest and therefore rate-limiting step for the process. Ethanol concentration varied during the process but as an average it remained within the range of 5% of the total carbon effluent and ~20–25% of the TOC detected in the system. Thus ~50% of the TOC is potentially due to other metabolic products. This could also explain the high discrepancy between the inlet and outlet carbon in some of the experimental points (Fig 3(A)). There are several different carbon sources present in the biomedium: EA, ethanol, acetic acid and/or other metabolic products, all of them easily biodegradable. This provokes the existence of a highly diversified and dynamic bacterial population (for example we observed that the biomedium colour varied continuously throughout the experiment). As a result the variations in the carbon content of the biomass could be quite considerable over time, while in the calculations it was considered constant and uniform.

For EA loadings higher than 550 g m^{-3} h^{-1} the dissolved oxygen concentration was lower than 1.4 mg O_2 L^{-1} and the process became oxygen limited. The oxygen limitation coincided with ethanol accumulation in the biomedium (ethanol concentration reached nearly 2 g L^{-1}) and a sharp decrease in EA removal efficiency (below 80%). When pure oxygen was fed to the bioreactor at a rate of 0.02 L min^{-1} the bioreactor recovered and could treat higher EA loadings without any oxygen limitation. Due to the fact that EA has high solubility in water (80.1 g L^{-1}),[24] the oxygen mass transfer limitation is an expected phenomenon for this process. To better assess this a theoretical study of the oxygen and the EA fluxes has been undertaken.

O_2 availability theoretical study

The volumetric mass transfer coefficient for oxygen ($K_L a_{O_2}$) was calculated based on the 'dynamic method of gassing out'.[18] The experiment was repeated three times and the average $K_L a_{O_2}$ value obtained was 63 h^{-1}. The oxygen flux in the biomedium is given by:

$$N_{O_2} = K_L a_{O_2} (C^*_{O_2} - C_{L_{O_2}}) V \quad (1)$$

where N_{O_2} is the oxygen flux, $C_{L_{O_2}}$ is the dissolved oxygen concentration, $C^*_{O_2}$ is the steady state saturated dissolved oxygen concentration and V is the biomedium volume. Thus, for a loading of 510 g EA m^{-3} h^{-1}, $K_L a_{O_2}$ 63 h^{-1}, $C^*_{O_2}$ 9.02 O_2 mg L^{-1}, $C_{L_{O_2}}$ 5.39 mg O_2 L^{-1} and V 1.1 L, the oxygen flux in the system was 7.86 mmol O_2 h^{-1}.

The EA flux, expressed in eqn (2), was calculated based on experimental data:

$$N_{EA} = GC_{in_{EA}} - GC_{out_{EA}} \quad (2)$$

where N_{EA} is the EA flux, while G and C represent the flow rate and the EA concentration in the gas streams; $GC_{in_{EA}}$ and $GC_{out_{EA}}$ are the influent and effluent EA rates. For G 2 L min^{-1}, $C_{in_{EA}}$ 4.68 mg EA L^{-1} and $C_{out_{EA}}$ 0.027 mg EA L^{-1} the EA flux was 6.4 mmol EA h^{-1}.

The yield factor for biomass production due to the substrate utilisation ($Y_{X/EA}$) has been also calculated. Thus, the yield factor is $Y_{X/EA}$ = 0.80 $g_{biomass}$ $g_{EA}{}^{-1}$ and because the molecular weight of bacteria is $MW_{biomass}$ = 25.5 $g_{biomass}$ $mol_{biomass}{}^{-1}$,[19] the molar fraction of the yield factor is $Y_{X/EA}$ = 2.76 $mol_{biomass}$ $mol_{EA}{}^{-1}$.

According to the EA oxidation reaction (eqn (3)), for every mole of EA dissolving in the biomedium, 2.07 moles of oxygen are needed for complete EA transformation to CO_2, H_2O and biomass.

$$CH_3COOCH_2CH_3 + 2.07O_2 + 0.69NH_3 \longrightarrow 1.24CO_2 + 2.28H_2O + 2.76CH_2N_{0.25}O_{0.5} \quad (3)$$

Thus, the theoretically calculated O_2 flux for complete biodegradation of the EA flux would be 13.18 mmol O_2 h^{-1}. On the other hand, the O_2 flux calculated from experimental data for a loading of 510 g EA m^{-3} h^{-1} was 7.86 mmol O_2 h^{-1}. The difference between the minimum demand of O_2 for complete mineralisation of the substrate and the O_2 flux calculated experimentally was 40%. This discrepancy between the theoretical and experimental O_2 fluxes was also confirmed by similar theoretical analysis based on the CO_2 produced from the process. For the specific EA flux, there was no oxygen limitation or significant ethanol accumulation observed. However, the oxygen limitation took place for a slight increase of the loading to 550 g EA m^{-3} h^{-1}.

There could be several possible explanations for the difference between the theoretical and experimental results of the O_2 analysis. One possible scenario could be that due to the fact that the biomass concentration was high (5–6 g L^{-1}) and the process was very 'intensive' (high stirring speed 800 rpm), the bacteria can utilise oxygen directly from the gas phase. Another is that the residual TOC and presence of ethanol indicates incomplete degradation, and so less oxygen is required than predicted by eqn (3)—although prior to the very high loading and concomitant generation of ethanol, the residual TOC values are only 10–15% of the carbon loading fed. The most possible explanation for the difference between the theoretical and experimental results is likely to be that photosynthetic microorganisms are growing in the culture. The bioscrubber was run twice under the same configuration and conditions to test repeatability. During the summer period that the first run took place the bioreactor was exposed to the sun/light and the biomedium had a green colour. The system showed an EA percentage removal higher than 96% for loading up to 550 g EA m^{-3} h^{-1} without any oxygen limitation, but due to a mechanical problem

it was decided to interrupt the experiment. During the second run, the bioreactor was not exposed to the sun/light and the colour of the biomedium was yellow. In this case, the system was oxygen limited at an EA loading of $550\,g\,m^{-3}\,h^{-1}$. Although microorganisms' specification has not been performed, due to the green colour of the biomedium during the summer period, maybe oxygen-producing photosynthetic bacteria were growing in the mixed culture, supplying in this way the biomedium with more oxygen than during the period that there was lack of sun/light, a fact that is in agreement with past studies.[25,26]

Biotrickling filter operation

During the first days of the BTF operation (Fig 1(B)), a technical problem occurred. The distribution nozzle placed at the top of the column, in order to distribute the biomedium evenly through the packing, was blocked due to the high biomass concentration. This fact resulted in a severe wall channelling of the biomedium in the column and very low removal efficiencies due to insufficient gas/liquid contact area.

The distribution nozzle was unblocked and slightly modified by increasing the hole-size and the removal efficiency of the BTF recovered. The EA loading increased over time in order to investigate the maximum elimination capacity of the BTF under the same operating conditions as the bioscrubber. Figure 2(B) presents the EA loading per unit volume of BTF per hour of operation and the EA percentage removal achieved. The removal efficiency was ~97–99% however, between 151 and 165 h the effluent EA increased due to NH_4^+ limitation of the culture, as detected by ion chromatograph analysis. Thus, the $(NH_4)_2SO_4$ concentration in the mineral medium was increased from $5000\,mg\,dm^{-3}$ to $10\,000\,mg\,dm^{-3}$ for the rest of the experiment and the effluent EA decreased at 194 h to low levels. As for the bioscrubber a carbon mass balance was performed using the same constituents (biomass, CO_2, TOC and EA in the gas outlet (ethanol concentration in the gas outlet stream was low and was not taken into account)). The carbon mass balance for the BTF closed pretty well, as can be seen from Fig 3(B). Again, as with the bioscrubber the main part of the carbon fed (87% as an average) was converted to biomass (measured in the recirculation tank) and carbon dioxide (Fig 4(B)). Interestingly the average percentage of carbon converted into biomass in the recirculation tank of the BTF was 40% while in the bioscrubber it was 36%. These numbers are pretty close and suggest that the main part of the biomass is actually growing in the recirculation tank rather than in the column. Thus it may be expected that the EA biodegradation occurs mainly in the recirculation tank as will be discussed later on. In the BTF system the ethanol concentration was carefully monitored in the gas and liquid phases from the beginning of the process. The concentration varied but again as an average remained within the range of 5% of the total carbon effluent (except for the starting up period) and 16% of the detected TOC. Similarly to the bioscrubber, acetic acid was not detected in the biomedium, however, NaOH was consumed, indicating acid production. Over the 5 days of operation, the system utilised $6.4\,mol\,EA\,m^{-3}\,h^{-1}$ ($560\,g\,EA\,m^{-3}\,h^{-1}$) and consumed $6.8\,mol\,NaOH\,m^{-3}\,h^{-1}$. Thus, the mass of NaOH consumed over that period was close to the amount needed stoichiometrically for the neutralisation of acetic acid produced. The maximum elimination capacity achieved was $600\,g\,EA\,m^{-3}\,h^{-1}$ with more than 97% removal. For higher EA loadings no nutrients or oxygen limitation was observed (at least the measured oxygen concentration was $\sim 3\,mg\,O_2\,L^{-1}$, eg still higher than the inhibitory level of $1.4\,mg\,O_2\,L^{-1}$ observed in the bioscrubber), but ethanol accumulated continuously in the biomedium. The last point of Fig 2(B) corresponds to an EA loading of $720\,g\,m^{-3}\,h^{-1}$, but although the EA percentage removal was 99% the ethanol concentration in the biomedium reached $1.8\,g\,L^{-1}$. Further operation of the system under these conditions resulted, as with the bioscrubber, in a decrease of the removal efficiency. The fact that the performance of both systems started deteriorating at ethanol concentrations of $\sim 2\,g\,L^{-1}$ suggests that this may be the inhibitory level for this mixed culture. From a practical point of view it is useful to show the elimination capacity of the bioscrubber and BTF as a function of the EA loading. The results presented in Fig 5 show that most of the experimental points are distributed around a straight line with a 45° slope, which indicates for complete EA removal in both systems.

From the analysis of the EA concentration in the inlet and outlet streams of the recirculation flow, the percentage of the EA loading degraded in the recirculation tank (vessel containing the biomedium recirculated through the column) was estimated. These results are presented in Fig 6 and varied a lot within the range of 56–96%. Thus, a significant fraction of the EA loading was degraded in the recirculation tank rather than in the BTF column.

As the bulk of the biodegradation was taking place in the biomedium, it is interesting to compare the two systems in terms of EA loading per volume

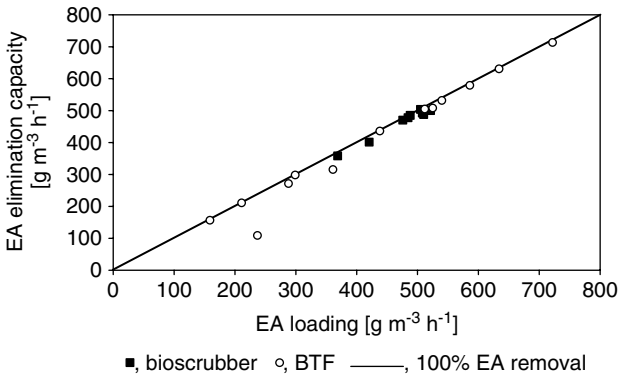

Figure 5. EA elimination capacity for different EA loadings in bioscrubber and BTF.

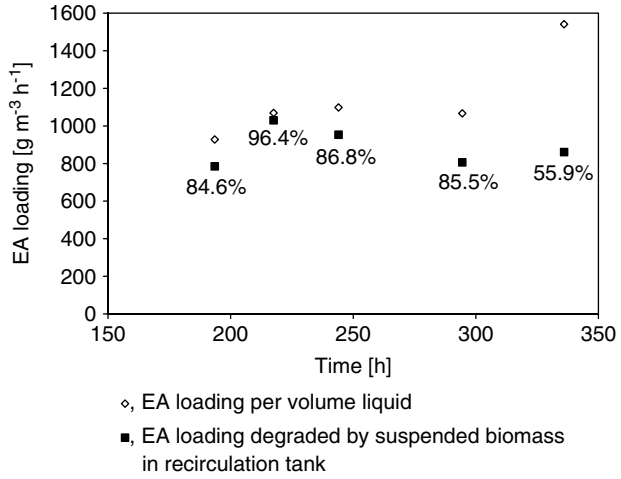

Figure 6. Percentage of the EA loading degraded by the suspended biomass in the BTF configuration.

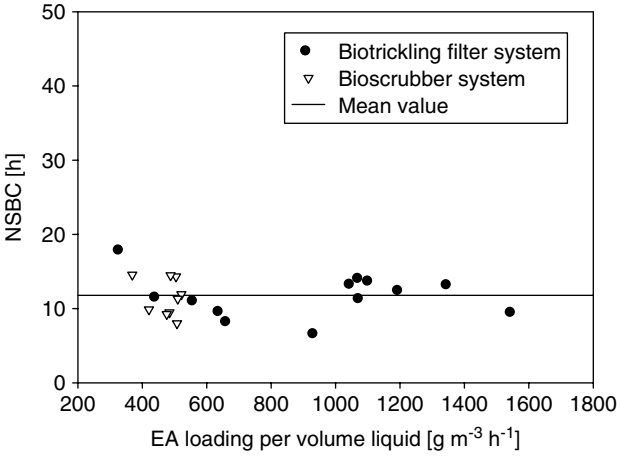

Figure 7. Normalised suspended biomass concentration (NSBC) in the bioscrubber and BTF (where NSBC = suspended biomass concentration [g m^{-3}]/EA loading per volume liquid [g m^{-3} h^{-1}]) as a function of the EA loading per volume liquid.

operating liquid. For the bioscrubber configuration it was observed that the biomass concentration was 5 g L^{-1} for an average loading of 500 g EA m^{-3} h^{-1}. In the BTF operation, the biomass concentration in the biomedium was 6 g L^{-1} for loading of ~300 g m^{-3} h^{-1} which corresponds to ~600 g m^{-3} h^{-1} EA loading per volume liquid. In the BTF system, by the end of the process the suspended biomass concentration reached levels as high as 15 g L^{-1} for EA loading of ~700 g m^{-3} h^{-1} (~1400 g m^{-3} h^{-1} loading per volume liquid). Figure 7 presents a normalised suspended biomass concentration (NSBC) in the bioscrubber and BTF (where NSBC = suspended biomass concentration [g m^{-3}]/EA loading per volume liquid [g m^{-3} h^{-1}]) as a function of the EA loading per volume liquid. Despite the data scattering it can be seen that the data points are distributed evenly around one mean value for both systems. These results confirm that the loading fed was utilised for the production of biomass mainly in the biomedium (suspended cells) of the recirculation tank, rather than to form a biofilm in the BTF column. The lack of thick biofilm formation in our system is probably due to the high liquid recirculation rate used, which effectively washes the biofilm from the packing. Comparison made with similar studies for EA removal indicates that indeed the recirculation rate/apparent liquid flow rate in our column is high. For example Lu *et al*[6] use a liquid flow rate of 0.02×10^{-4} m s^{-1}; Kozliak *et al*[27] 0.29×10^{-4} m s^{-1} and 0.83×10^{-4} m s^{-1} while in our system the apparent liquid flow rate is 18.89×10^{-4} m s^{-1}. On the other hand this result gives a useful hint for further studies. By careful optimisation of the liquid flow rate through the column the biofilm thickness could be controlled and clogging of the biotrickling filter prevented. However the high suspended biomass concentration was still generating problems with the uniform distribution of the liquid through the packing and gas and liquid channelling was observed. The high liquid flow rate used could also improve the mass transfer in the column, which led to the observed very high removal efficiency.

Table 1. Literature data for degradation of EA gas in different biological systems

Reference	EA loading rate	EA removal (%)
Liu *et al*[4] (2002) (biofilter)	450 g m^{-3} h^{-1}	~90
Chang *et al*[3] (2001) (biofilter)	18–153 ppmv	~83
Lu *et al*[6] (2001) (BTF)	>490 g m^{-3} h^{-1}	~95
	>810 g m^{-3} h^{-1}	~90
Deshusses *et al*[5] (1999) (BTF)	200 g m^{-3} h^{-1}	~80
This study: bioscrubber	550 g m^{-3} h^{-1}	~96
biotrickling filter	600 g m^{-3} h^{-1}	~97

The results of the present study have been compared with the results from previous studies[3–6] for the treatment of EA vapour. Data that have been collected for EA degradation in biological systems are presented in Table 1. From the table presented above, only Lu *et al*[6] is close to the EA elimination capacities and the percentage removal achieved by the bioscrubber of the present study. The biomass growth and the elimination capacities achieved in the recirculation tank of the BTF set-up indicate that if the oxygen mass transfer is enhanced, the bioscrubber system would be able to perform much higher removal efficiencies for loadings even in the range of 1400 g m^{-3} h^{-1}. None of the above studies could demonstrate such high EA removal efficiency.

CONCLUSIONS

Overall the performance of the two systems was similar. The maximum elimination capacities and the percentage removals achieved were very close. On the other hand, the enhancement of the oxygen mass transfer that the BTF column provided, resulted in an extensive suspended biomass growth in the recirculation tank (up to three times higher biomass

concentrations than in the bioscrubber) and the ability to biodegrade up to three times higher EA loading per volume liquid. This result indicates that the bioscrubber system still has a large unexploited potential. From an engineering point of view the bioscrubber is a much more reliable system in terms of construction operation and control. Its performance could be improved by enhancing the mass transfer between the gas and liquid phase. Such an enhancement is possible with the introduction of a low flow rate of pure oxygen or the introduction of a venturi eductor for better mixing of the two phases.

A careful optimisation of the liquid flow rate through the biotrickling filter column could be used as a tool for biofilm thickness control and biotrickling filter clogging prevention. This could also improve the system removal efficiency by increasing the mass transfer rates.

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